CRYSCOR07

Beta Version 0.94

User's Manual

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Contents

1 Introduction **2**
- 1.1 Functionality . . . 2
- 1.2 How to run CRYSCOR . . . 2
- 1.3 Notes on the Beta Version . . . 3
- 1.4 Acknowledgments . . . 3

2 Input instructions **4**
- 2.1 Input format . . . 4
  - 2.1.1 Typographical conventions and acronyms . . . 5
- 2.2 Symmetry adapted WnF . . . 6
- 2.3 General CRYSCOR keywords . . . 8
- 2.4 Truncation criteria and tolerances . . . 8
- 2.5 Active Space . . . 8
- 2.6 WnF domain definition . . . 9
  - 2.6.1 General definition . . . 9
  - 2.6.2 DOMCOE . . . 9
  - 2.6.3 DOMPUL . . . 10
  - 2.6.4 DOMDEF . . . 10
  - 2.6.5 MOLDOM . . . 10
  - 2.6.6 TESTDOM . . . 10
- 2.7 Dual Basis Set . . . 11
  - 2.7.1 GUESSDUA . . . 11
  - 2.7.2 DUALBAS . . . 12
- 2.8 MP2 Equations . . . 13
- 2.9 MP2 Energy . . . 14
  - 2.9.1 Pairs Partitioning . . . 14
  - 2.9.2 Freezing of Indices . . . 14
- 2.10 Beyond MP2 energy . . . 15
- 2.11 Two-electron integrals . . . 16
  - 2.11.1 Exact two-electron integrals . . . 16
  - 2.11.2 Multipolar Expansion . . . 16
  - 2.11.3 Density Fitting . . . 16
- 2.12 Printing and plotting . . . 16

A Input Examples **18**

B Output Examples **20**
- B.1 Commented Output . . . 20
- B.2 Lennard-Jones contribution . . . 26

Chapter 1

Introduction

CRYSCOR is a **post Hartree-Fock** (HF) **local** correlation program for non-conducting crystals[1].
It can be considered as the post-HF option of the CRYSTAL program[2], since the good reference HF solution for the crystalline systems is provided by this code.
The post-HF method currently implemented is a perturbative method, namely Møller-Plesset at the second-order (MP2). Well localized symmetry adapted Wannier functions[3, 4] (WnF) are adopted instead of delocalized Bloch functions; this permits the exploitation of the **short-range** nature ($E \propto R^{-6}$) of electron correlation following the general Pulay scheme[5] as implemented in the molecular MOLPRO code[6]. Its generalization to periodic 3-dimensional systems requires a full use of both point and translational symmetry.
Actually, the localization procedure and the MP2 method itself are not suitable for conducting systems.

1.1 Functionality

- density fitting technique for the evaluation of 2-electron integrals[10, 11];
- use of dual basis-set;
- evaluation of long-range energy contributions by means of Lennard-Jones extrapolation technique;
- two different schemes to perform the MP2 correction to HF density matrix[12, 13];

1.2 How to run CRYSCOR

To execute a CRYSCOR job, you ought to run before two CRYSTAL calculations (for more details about the CRYSTAL code please refer to *Crystal User's Manual* [7] and CRYSTAL web site: www.crystal.unito.it).
On Unix systems, CRYSCOR (and CRYSTAL) is accessed using directly the **cryscor** executable (**crystal**, and **properties**). Syntax and procedure are outlined in the following paragraphs.

A. **crystal** executable performs a wave function calculation. Geometry and symmetry information, Fock and density matrix, canonical eigenvalues and eigenvectors are stored on fortran unit $fort.9$, that must be saved at the end of the run.

crystal < *crystal_input*12_*filename* > *crystal_output*12_*filename*

B. **properties** executable calculates on request a number of quantities of interest. By means of the `LOCALI` keyword, localized Wannier functions (WnF) are calculated from the subset of occupied (delocalized) crystalline orbitals and symmetrized [9] (keyword `SYMMWF`). The related information is stored in fortran unit *fort*.80, that must be saved at the end of the run.

properties < *crystal_input*3_*filename* > *properties_output*3_*filename*

C. the CRYSCOR calculations are to be run, in the directory containing the *fort*.9 and *fort*.80 fortran units, as follows:

cryscor < *cryscor_input_filename* > *cryscor_output_filename*

Suggested file extensions for input and the output are summarized in table 1.1.

executable	input file	output file	data saved
crystal	.d12	.out	.f9
properties	.d3	.outp	.f80
cryscor	.d4	.outc	.f84, .f91 (sec. 2.11); .f131 (sec. 2.9.2)

Table 1.1: Input and output standard file names.

1.3 Notes on the Beta Version

♣ CRYSCOR is linked to the public version of CRYSTAL: pub_1_0_1. With respect to the standard release, this source contains the DUAL BASIS option (see manual 2.7.2) and an update version of the *localy_sym* subroutine.

♣ The density fitting option is in progress: a reliable version will be provided soon.

1.4 Acknowledgments

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Chapter 2

Input instructions

2.1 Input format

The Input consists in a series of keywords (KW) possibly followed by the respective arguments, to be written in separate cards (card 1, card 2, ...) in free format, as shown in the following sections.
Not all KWs are necessary; the ones that are mandatory are marked as **KM**, the others as **Ko**. The ones marked with **KT** are technical keywords, used by the developers of the code.
For the parameters defined by optional Keywords (Ko), default values are provided by CRYSCOR, as indicated in square brackets. A typical CRYSCOR input file looks as follows (table 2.1): the order of KWs is practically free, but some conditions must be

```
NEWK          ⟶ CRYSTAL eigenvalue calculation
12 12 12
0 0
MEMORY        ⟹ Memory required (kbytes)
1200000
DOMDEF        ⟹ Definition of the virtual space
1
1 3
1 2 3
PAIR          ⟹ Definition of the occupied space
2 2
TOBJ          ⟹ Tolerances
0.01 0.01
END
END
```

Table 2.1: CRYSCOR input sample.

respected, e.g.:

1. `NEWK` must be the first Input card;
2. `MEMORY` must be the second keyword;

3. `DFCHECK` requires `DFITTING` to be present and exact integrals to be available on F84 unit;

4. `INTREA` requires integrals to be available on F84 unit;

5. `AMPREA` requires amplitudes to be available on F91 unit;

The description of the input is subdivided into sections which control different parts of the code. Inside each sections, the meaning of KWs and of the respective parameters is summarily indicated in an input deck; then, detailed explanations, suggestions and comments are added and some input examples are provided.

2.1.1 Typographical conventions and acronyms

In the description of the input data which follows, the following *typographical conventions* are adopted:

- • new record
- [ ] default values.
- { } suggested values.

Moreover, some *acronyms* will be used:

-	**AO**	Atomic Orbital, centered on atom, obtained as a linear combination of Gaussian type orbitals (GTO)
-	**WnF**	Wannier Functions, basis set of the occupied manifold
-	**WnFf**	Flower of Wannier Functions: group or single WnF which form a basis for a representation of point group operators and share the same center [9]
-	**PAO**	Projected Atomic Orbitals, basis set of the virtual space
-	**FF**	Fitting Function for the Density Fitting approximation of two-electron integrals

2.2 Symmetry adapted WnF

An input file for the **properties** part of CRYSTAL (namely, those with the extension *d*3, see section 1.2, step **B** and table 1.1) has to be prepared in order to obtain well localized and symmetry adapted WnFs. The definition of WnFs is controlled by an input block, opened by **LOCALWF** and containing a set of keywords, as **VALENCE**, explained in the *Crystal User's Manual*[7].
The *a-posteriori* symmetrization procedure, mandatory in the case of a subsequent MP2 calculation, is activated by **SYMMWF**. The procedure[9] can be briefly outlined as follows:

1. WnFs are classified depending on the number of atoms that most contribute to it, on the basis of the atomic population analysis; in particular, WnFs will be defined *bond* or *atomic* if the charge density is mainly concentrated on one or two atoms, respectively. These atoms will be referred in the following as "main" atoms.

2. according to both shell population and symmetry properties of the main atoms, WnFs are grouped into subsets;

3. the symmetry of each subsets is verified;

4. in the case of subsets composed of non-symmetry related WnFs, the WnFs are projected into the sub-space defined by the point group of the subsets (a sub-group of the crystal point group). Each WnF becomes a representative function of one of the rows of the irreducible representation (IRREP) of the sub-group.

5. As a result of this procedure, each WnF is classified by four index (b,f,p,g) [bunch, flower, petal and crystal cell] such that a general symmetry operator $\widehat{W}$ of the crystal applied to a WnF gives:
   $\widehat{W}$ (b,f,p,g) $= \sum T^{W}_{pp'}$ (b,f^{W},p',g^{W})

A new set of optional keywords permits us to control and optimize the procedure, so that an input file (for the acetyl crystal) can look like this:

```
NEWK
4 4 4
1 0
LOCALWF                    # begin of the localiz.[
SYMMWF                     #( the symm. adap. proc. is switch on
END                        #) end of the symm. input block
VALENCE                    # localiz. keywords
CYCTOL                     #
2 3 4                      #
BOYSCTRL                   #
8 8 100                    #
WANDM                      #
-2 4 1                     #
FULLBOYS                   #
6                          #
END                        #] end of the local. input block
END                        # end of the properties input block
```

rec	variable	value	meaning
•	A8 **SYMMWF**	Ko	symmetry adaptation of WnFs
•	A8 **SYMMFLAG**	Ko	activate symmetrization options
•	I IFSYM	[0]	Foster-Boys loc. procedure followed by WnFs symmetry adap.
		1	WnFs symmetry adaptation and then Foster-Boys loc. procedure
		2	read WnFs from a previous run, (*fort.88*)
	I IFSAVE	[0]	default value
		1	save WnFs on fortran unit *fort.88*
		2	after symm. adap., do not perform the re-wannierization step
		3	after symm. adap., do not perform the re-wannierization and re-orthogonalization steps
•	A8 **TOLBON**	Ko	redefinition of the tolerance to classify WnFs as *bond* or *atomic*
•	F TOLB	[0.2]	if $abs[pop(1) - pop(2)] < tolb$ then it is a *bond* WnF, where *pop* is the atomic population and 1, 2 are the two main atoms
•	A8 **SYMVER**	Ko	WnF symmetry is verified by means of scalar products performed in a number of crystal cells defined by **g**-max
•	I MMG	[MMMG0]	value of **g**-max
•	A8 **PRINT**		define the level printing level
•	I NPRINT	[1]	
•	A8 **END**		end of SYMMWF block

With reference to the input file, some comments can be done.

- The last two options of the **SYMMFLAG** keyword, (`IFSAVE=2,3`) are intended to maximally preserve the WnF symmetry, to a small detriment of the local character.

2.3 General CRYSCOR keywords

rec	variable	value	meaning
• A8	**NEWK**	KM	CRYSTAL HF eigenvectors calculation at a number of **k** point in the reciprocal space
• I	IS		shrinking factor for reciprocal space net (Monkhorst net). The number of **k** points, where the Fock/KS matrix is diagonalized, is roughly proportional to IS^{IDIM}/MVF where IDIM denotes the periodic dimensionality of the system, and MVF denotes the number of point symmetry operators.
I	ISP		shrinking factor of the secondary reciprocal space net (Gilat net) for the evaluation of the Fermi energy and density matrix.
• I	IFE	{0}	no Fermi energy calculation is performed;
		1	Fermi energy is computed, by performing integration on the new **k** points net.
	NPR		number of printing options to switch on (not active)
• A8	**MEMORY**	KM	memory allocation
• I	IMEM		allocation in KBytes
• A8	**PGNEW**	Ko	recompute the CRYSTAL Density Matrix P^g according to the given tolerance
• F	EXAD		adjoned GTF exponent for P^g truncation
• A8	**WPROJE**	KT	density matrix P^g from PAO projection
• A8	**END**	KN	to end main input stream

2.4 Truncation criteria and tolerances

rec	variable	value	meaning
• A8	**CONTOL**	Ko	SCF convergence criteria
• I, F	MAXC CONV	[10, 0.000001]	Max. number of cycles; tol. on energy difference (Ha)
• A8	**TOBJ**	Ko	Truncation of WnFs and PAOS
• 2F	TWF, TPAO	[0.001, 0.001]	
• A8	**PAIR**	Ko	strong/weak/distant WW pairs
• 2I	DIST1,DIST2	[5, 11]	$0/0 \div d_1/d_1 \div d_2$: d_1, d_2 (Å)
• A8	**COREQ**	Ko	exclude "evanescent" PAOs
• I	JNORM	[1]	elimin. PAOs with norm$< 10^{-\mathrm{JNORM}}$
• A8	**LONTOL**	Ko	truncation of LON
• F	TOLS	[0.01]	tolerance on the LON overlap matrix
• A8	**DELPAO**	Ko	exclude the selected PAOs from the virtual space
• I	N		num. of PAOs to eliminate
• M	NP=1,N		PAOs to eliminate

2.5 Active Space

These keywords reduce the dimension of the active space, that is the extension of the crystalline system, with a sensitive saving of computational cost. However, both the keywords are delicate, especially in the case of periodic Density Fitting (DFP).

	rec	variable	value	meaning
•	A8	**OPERTOL**	Ko	active region
•	F, I	TOLOR NFAC	[0.01, 6]	tolerance for cutting the coefficients; multiplication factor for the distance
•	A8	**STAR**	Ko	MMMG0 redefinition
•	I	NSTAR		n. star of g-vectors

2.6 WnF domain definition

The definition of the WnF domains that is, the atoms and, consequently, the PAOs associated to each WnF, is crucial to the accuracy and cost of the calculation. Several definitions are possible. Note however that WnFs which belong to the same "flower" have the same domain. Therefore, the definition concerns only the different flowers; their reference number and the relevant information is printed by PROPERTIES, at the end of the localization procedure (look at the string `WnF INFORMATION`).
Several possibilities exist to properly define the WnFf domains, as will be commented in the paragraphs below.

2.6.1 General definition

Flower domains can be defined according to different criteria:

- atomic coefficients in the WFs expansion (DOMCOE) see 2.6.2
- atomic population in the WFs (DOMPUL) see 2.6.3
- atom distacences from the WF centroids (DOMDEF) see 2.6.4
- molecular domain (MOLDOM) see 2.6.5

In all the cases, flower *kernel* domains are defined and used for the generation of WW-pairs. According to the *ATOMIC* or *BOND* flower character, these domains contain one single atom or the two atoms involved in the bond, respectively.
There are two general keywords:

	rec	variable	value	meaning
•	A8	**MINPOP**	Ko	Design minimal domains, used in the generation of **WW-pairs**
•	F	mindom_pop	[0.1]	only those atoms are included whose WnF population is > mindom_pop
•	A8	**MAXDOM**	Ko	Setting the maximal number of atoms in the WnFf domains
•	F	maxdom	[60]	maximal number of atoms that can be included in a single WnFf domain

2.6.2 DOMCOE

The domain of the i-th WnF is specified as comprising all atoms which contain at least an AO χ_μ such that the coefficient $c_{\mu,i}$ is larger in absolute value than a prescribed value: by default, `TDOM`=0.01. `TDOM` can be changed by activating the keyword `DOMCOE`. This default setting is usually inadequate; on the other hand, assigning very low values to `TDOM` may lead to domains which are too large (with very high computational cost) or have strange shapes.

rec	variable	value	meaning
• A8	**DOMCOE**	Ko	standard domains: DEFAULT
• F	TDOM	[0.01]	include atom if at least one of its coeff. is > TDOM

2.6.3 DOMPUL

A definition which is chemically more sensible is provided by the Boughton-Pulay (BP) criterion: a sort of "Mulliken population analysis" is performed for each WnF, by looking how much of it (out of a total of 1) is "provided" by the different atoms; these are included in the domain in order of decreasing contribution, until the domain contains a preset fraction (`WFPOP`) of the total WnF population. Note that atoms which are equivalent by symmetry with respect to the WnFf, and contribute therefore the same population, are all included in the domain (or all excluded). The BP criterion is adopted by activating the keyword `DOMPUL`.

rec	variable	value	meaning
• A8	**DOMPUL**	Ko	Boughton-Pulay (BP) domains
• F	WFPOP	[0.98]	total WnF pop. in BP domain

2.6.4 DOMDEF

A more specific tailoring of WnFf domains is possible by activating the following keywords. For each WnFf, stars of equivalent atoms are included in the domain; the total number of stars and the "identification labels" of the different stars included (in order of increasing distance from the WnFf center) are indicated by the variable `NSTAR` and the vector `ISTAR`, respectively (see examples in the Appendix).
A very useful keyword, in the case of **molecular** crystals is `MOLDOM`; for each WnF it defines, on the basis of atomic connectivity, a domain corresponding to the molecular unit.

rec	variable	value	meaning
• A8	**DOMDEF**	Ko	Design WnFf domains by **stars** of atoms
• I	NWFDOM		number of WnFf domains to define
	for each WnFf N=1,NWFDOM insert the following keywords:		
• 2I	NWF NST		Which WnFf, n.stars to be included
• 20I	ISTAR=1,NST		which stars of atoms (according to a distance criteria with respect to the WnFf center)
• A8	**DOMDEF2**	Ko	Design WnFf domains by **atoms**
• I	NWFDOM		number of WnFf
• 20I	IATS=1,NWFDOM		how many atoms (closest to the WnF's centers) to be included in the domains. If needed, additional atoms are automatically added to fill the stars of atoms.

2.6.5 MOLDOM

Recommended for molecular crystals.

rec	variable	value	meaning
• A8	**MOLDOM**	Ko	molecular domain

2.6.6 TESTDOM

It may sometimes be useful to have a preliminary look at the possible shapes of the domains without performing a calculation. This possibility is provided by activating

the keyword TESTDOM. The coordinate and types of the atoms in each domain are stored on Fortran unit 17 in xyz format for visualization, and the computation stops. Moreover, the composition of the different stars, their distance from the WnFf center etc., are printed in the output file so allowing further selection (look at the string DOMAIN INFORMATION). Two choices are possible. Either the same number of stars and the same sequence are used for each domain (keyword ALLEQ), or differences are allowed between the different domains (keyword NONEQ). In the former case, only one variable NSTAR and one vector ISTAR must be defined. In the latter case, domains are generated following the same criterion as for DOMDEF.

rec	variable	value	meaning
• A8	**TESTDOM**	Ko	Test run for WnFf domains domain, STOP after defining WnFf domains
	insert one of the following set of cards, I or II:		I
• A8	ALLEQ		all WnFf domains are equal
• I	NWFDOM		N. WnFf domains to define
• I	NSTAR		number of.stars
• 20I	ISTAR=1,NSTAR		which stars from WnFf center
	or		II
• A8	NONEQ		different WnFf domains
• I	NWFDOM		N. WnFf domains to define
	for each WnFf N=1,NWFDOM insert the following keywords:		
• 2I	NWF NSTAR		Which WnFf, nunmber of stars
• 20I	ISTAR=1,NSTAR		Which stars from WnFf center

2.7 Dual Basis Set

In the study of extended systems, the use of diffuse basis sets is limited by the incoming of linear dependencies in the overlap matrix. On the other hand, a correct description of the virtual manifold, often achieved with extended basis sets, plays a crucial role in electron correlation calculations. To overcome this problem a *dual basis set* option has been implemented, in which two different basis set are used; the first one, called **ref**, is used for the calculation of the HF reference solution (that is to generate the WFs); the second one, improved with as many diffuse functions as we want, called **mod**, is used in the correlation calculation (to generate PAOs and to perform the MP2 equations). The procedure is the following:

1. a CRYSTAL+PROPERTIES calculation with the **ref** basis set to obtain the reference WFs (fort.80);
2. a CRYSTAL calculation with the **mod** basis set and the **GUESSDUA** keyword on (see 2.7.1) to get all the quantities of interest in the new basis set (fort.9);
3. a CRYSCOR calculation with the **DUALBAS** keyword on (see 2.7.2 for details).

2.7.1 GUESSDUA

The keyword GUESSDUA is a [1] restart option of CRYSTAL that could be useful in the following cases:

[1] A. Meyer, "Simulazione di epi-layer ossidici su superfici metalliche con tecniche quanto-meccaniche periodiche, 2006/2007, Thesis.

- in a basis set optimization procedure;
- to improve the virtual manifold description without modifying the HF (or DFT) solution.

The last item refers to the possibility of freezing the SCF procedure (no need to go to convergence), and is essential for CRYSCOR. It can be activated by inserting in the third (last) CRYSTAL input block the keyword as follows:

	rec	variable	value	meaning
•	A8	**GUESSDUAL**	Ko	activate the option
•	2I	NFRAG		number of insertions, as classified below
		CYCLZ		0 for a complete calculation and 1 if the calculation is stopped at the zero-cycle (no diagonalization of the Fock matrix is performed)
		for each I=1,NFRAG insert the following keywords:		
•	NI	IRRAT(I)		label of the irreducible atom (geometry input order) whose basis is changed
		STSH(I)		number of the shell of the atom IRRAT(I) after which the insertion is made
		NUMSH(I)		number of shells added (if NUMSH is positive) or deleted (if NUMSH is negative) after the shell STSH(I)

WARNING! - Note that being a restart option, the GUESSDUA keyword needs the fortran unit *fort*.20, which is a copy of the *fort*.9, to restart the calculation of the modified basis from the original one.
WARNING! - To run a CRYSCOR calculation, the GUESSDUA option has to be used by freezing the SCF procedure at the zero-cycle (CYCLZ=1).
For further information on the GUESSDUA option refer to the CRYSTAL[2] manual.

2.7.2 DUALBAS

The dual basis set option in CRYSCOR is activated by the keyword DUALBAS: it is mandatory to put the **DUALBAS** keyword **before the NEWK** one.
To run a MP2 calculation the following fortran units have to be provided:
- the fort.9 unit of the **modified** calculation,
- the fort.80 of the **reference** one.

	rec	variable	value	meaning
•	A8	**DUALBAS**	Ko	activate the option

2.8 MP2 Equations

rec	variable	value	meaning
• A8	**MP2OLD**	KT	Invoking the old code for the equations
• A8	**NOSYM12**	KT	Switching off the symmetry i with respect to permutations of the WnFs i and j in the (ij) pairs
• A8	**EQALG**	KT	Evaluation of the beta terms in the LMP2 equations
• I	int_alg	[2]	Algorithm 1 or 2
• A8	**TOLEQPRS**	KT	Prescreeining in the evaluation of the beta terms in the LMP2 equations
• F	thr_eq	[10^{-8}]	Threshold for prescreeinig
• A8	**TOLEAMPS**	KT	Prescreeining for evaluating the updates in the LMP2 equations
• F	thr_eq2	[10^{-8}]	Threshold for prescreeinig

2.9 MP2 Energy

2.9.1 Pairs Partitioning

rec	variable	value	meaning
• A8	**MOLATOMS**	Ko	Activating the partitioning of the crystal into "molecules" and "environment"
• I	n_molpairs	[0]	number of atoms which are considered to be "molecules"
• nI	i_mol=1,n_molec		the list of the atoms belonging to the "molecules"
• A8	**MOLPAIR**	Ko	strong/weak/distant WW pairs with both WnFs having at least one "molecule" atom in their domains each ("molecule" WnFs)
• 2F	DIST1 DIST2		$0 \div d_1/d_1 \div d_2/d_2 \div \infty$: d_1, d_2 (Å). If DIST1 DIST2 are 0, no pairs of this type are included
• A8	**ENVPAIR**	Ko	strong/weak/distant WW pairs, where both WnFs do not have the "molecule" atoms in the domains ("environment" WnFs)
• 2F	DIST1 DIST2		$0 \div d_1/d_1 \div d_2/d_2 \div \infty$: d_1, d_2 (Å). If DIST1 DIST2 are 0, no pairs of this type are included
• A8	**MOENPAIR**	Ko	strong/weak/distant WW pairs between the "environment" and "molecule" WnFs
• 2F	DIST1 DIST2		$0 \div d_1/d_1 \div d_2/d_2 \div \infty$: d_1, d_2 (Å). If DIST1 DIST2 are 0, no pairs of this type are included

2.9.2 Freezing of Indices

All these keywords can be used for consistency in geometry optimization and work correctly if the order of WnFs in different geometries is the same.

rec	variable	value	meaning
• A8	**FIXDOM**	Ko	Saving the information on the domains and on the number and type of the pairs in the file fort.131.
• A8	**FIXNPAOS**	Ko	Saving the number of the redundant PAOs for each pair in the file fort.132.
• A8	**DOMREA**	Ko	Reading the information on the domains and on the number and type of the pairs from fort.131.
• A8	**NPAOSREA**	Ko	Reading the number of the redundant PAOs for each pair from fort.132
• A8	**DOMONLY**	Ko	Does not perform the actual LPM2 calculations. Obtains the information on the domains, pairs, redundant PAOs and stops

2.10 Beyond MP2 energy

rec	variable	value	meaning
•	A8 **PCALC**	Ko	MP2 Density matrix
•	2I IFFPAIR TOL_P		n. of WnFf pairs in local space and Tol. on Wannier coeff.
•	A8 **DENSMAT**	Ko	LMP2 Lagrangian orbital-nonrelaxed Density matrix
•	F THR_DENS	$[10^{-8}]$	tolerance for evaluating the density matrix
•	A8 **LENJONES**	Ko	Lennard-Jones contribution to energy
•	F (d_1 <) DLJ1 (< d_2)		only reducible WFf-pairs with distance from the reference cell greater than DLJ1 and lower than d_2 are used to calculate the L-J coeff.
	F DLJ3		the contribution from all flower pairs between d_2 and DLJ3 is evaluated
	F TOLLJ	[20]	L-J calculation stops when the k-th g-star's energy contrib. is smaller than $1.^{-tollj}$
	I IPRINT	1	level of printing

2.11 Two-electron integrals

2.11.1 Exact two-electron integrals

rec	variable	value	meaning
• A8	**SCHWARZ**	Ko	2-el integrals Schwarz screening
• 3I	TS1 TS2 TS3	[10 10 10]	Schwarz tolerances (10^{-TS}
• A8	**DSCREEN**	Ko	2-el integrals coeff. pre-screening
• 3I	TD1 TD2 TD3	[4 4 4]	Density screening tolerances (10^{-TD})
• A8	**INTREA**	Ko	Read integrals from fortran unit *f84*
• A8	**AMPREA**	Ko	Read amplitudes from fortran unit *f91*
• A8	**ASYMDOM**	Ko	only vertical excitations are considered

2.11.2 Multipolar Expansion

rec	variable	value	meaning
• A8	**MULTIPO**	Ko	Multip. calc. of 2-el intgrls for $d_1 \leq d_{\mathrm{WW}} \leq d_2$
• I	NMULTIP	{4}	Max multipole moment
• A8	**MULTDIST**	Ko	optional redef. of d_1
• F	DIST1	[4.]	d_1 (Å)

2.11.3 Density Fitting

For the DF theory in CRYSCOR, see reference [10, 11, 15].

2.12 Printing and plotting

It may be useful to obtain printed or graphical information on some quantities of interest. Here are some suggestions for the use of the printing options.

The `IPRINT` variable controls the general level of printing. It is advisable to keep it at its default value (1). If `IPRINT` is set to > 1, however, ...

Detailed information on some specific items can be collected if **one** of the following KWs (general name `item`) is activated after the `IPRINT` card:
`WF FWF PAO SPAO FPAO LON SLON FLON` as illustrated below. An `item=END` card must be inserted to end the printing section of the Input, either immediately after the `IPRINT` card, or group of the other `item`'s cards.

rec	variable	value	meaning
•	A8 **PRINPLOT**	Ko	Define printing options
•	I IPRINT	[1]	General level of printing
•	A8 "item"	Ko	Print/plot info on `"item"`: `END WF FWF PAO SPAO FPAO LON SLON FLON DOMAIN`
			if item=END, then end print sect., else read in a sequence
•	2I NPRG IGPLT		the AOs coeff. of $NPRG$ crystal cells are printed in the output file; n. of star of g-vectors to be used in the plot (data stored on $fort.25$)
•	nI NG(1) NG(2)...		selected crystal cells for the printing option
			if IGPLT≠ 0 then insert **MAPNET cards** *(see also Crystal User's manual[7])*
•	I3 NPY		number of points on the B-A segment.
			enter a keyword to choose the type of coordinates I
•	COORDINA		
•	∗ XA,YA,ZA		cartesian coordinates of point A
•	∗ XB,YB,ZB		cartesian coordinates of point B
•	∗ XC,YC,ZC		cartesian coordinates of point C
			or I
•	ATOMS		
•	∗ IA		*label* of the atom at point A
	AL,AM,AN		indices (direct lattice, input as reals) of the cell where the atom is located
•	∗ IB		*label* of the atom at point B
	BL,BM,BN		indices (direct lattice, input as reals) of the cell where the atom is located
•	∗ IC		*label* of the atom at point C
	CL,CM,CN		indices (direct lattice, input as reals) of the cell where the atom is located

Appendix A

Input Examples

1. Input barebone

```
NEWK
8 8 8        # Monkhorst shrinking factors for CRYSTAL eigenvalues calculation
1 0          # Fermi Energy recalculation and no printing option switched on
MEMORY
1000000
END
```

2. Suite Input

```
NEWK
16 16 16
0 0
MEMORY
1000000
COREQ
1
CONTOL
10 0.0001
DOMPUL
0.98
PAIR
4. 4.
TOBJ
0.005 0.005
SCHWARZ
8 8 8
DSCREEN
8 8 8
END
```

3. Input for the Domain definition

```
NEWK
8 8 8
1 0
MEMORY
1000000
DOMDEF
ATOMS                                   # domain are defined in terms of atoms
16                                      # number of flowers
1 15                                    # first flower, 15 atoms
1 2 3 4 5 6 7 8 9 10 11 12 14 15 16     # selected atoms: in distace order from the
                                        # flower centroid
2 15
1 2 3 4 5 7 8 15 16 10 24 27 23 26 29
3 15
.....
16 15
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
PAIR
4. 6.
TOBJ
0.005 0.005
END
```

4. Printing and Plotting Input

```
PRINPLOT
1            # Level of printing
WF           # KW=WnF: printing and plottinf of the Wannier functions
4 3          # AOs coef. are printed in 4 g-vectors;
             # WnFs are plotted including AOs coef. of the first 3 stars of g-vectors
1 2 5 8      # selected g-vectors (printing)
END
60           # see CRYSTAL manual MAPN option
ATOMS        #
1 0 0 0      #
2 0 0 0      #
1 1 1 0      # end of CRYSTAL MAPN option
END
END
```

5. Density Fitting Input

```
....
DFITTING                          # Input for DF estimate of LiF integrals
8                                 # shrinking factor of k-net for DF FT
12                                # fitting radius (A)
STDBASIS                          # Basis Set  Input Card
VTZ                               # Basis Set type
ENDDF                             # End of DF Input deck
....
```

Appendix B

Output Examples

B.1 Commented Output

In the following, we comment the output files of two MP2 calculations for an acetyl (**ACE**) and a Lithium hydride (**LiH**) crystal, respectively. The former one refers to a rather complicated system, and poor tolerances are adopted; the latter one is extremely simple, and the computational conditions are very good. These two cases will allow us to comment on specific aspects of the output files.
ACE is a molecular crystal of cubic symmetry (space group *pa3*) comprising four acetylene molecules (HC≡CH) per unit cell. All C and H atoms are symmetry equivalent to each other. The basis set adopted for C comprises one s, two sp and one d shell; for H, two s and one p shell.
LiH is an ionic crystal of cubic symmetry (rocksalt structure, space group $Fm\overline{3}m$), with only one lithium and one hydrogen per cell. The basis set adopted for Li comprises two s, one p and one d shell; for H, three s, one p and one d shell.
The two CRYSCOR calculations are performed with the following inputs:

```
#ACE
NEWK
8 8 8
0 0
MEMORY
10000000
COREQ
1
CONTOL
50 0.00001
MULTIPO
4
PAIR
4. 6.
MOLDOM
TOBJ
0.01 0.01
SCHWARZ
8 8 8
DSCREEN
8 8 8
PRINPLOT
1
END
END
```

```
#LiH
NEWK
8 8 8
0 0
MEMORY
1200000
DOMDEF
1
1 3
1 2 3
DFITTING
8
20 40
1 12
0 0 1 1
 4.242065   1.
 [ .. density fitting basis set .. ]
99 0
END
0.001 0.001
ENDDF
MULTIPO
4
PAIR
8. 12.
TOBJ
0.001 0.001
END
```

***** General information *****
In the output, the number of AOs and WnFs is first reported, followed by a list of the most important CRYSCOR parameters adopted in the calculation.
The case of **ACE** is reported below:

```
-------------------------------------------------------------------------------
*** MP2 CORRELATION ENERGY ***

 Number of AOs: 152
 Number of WFs:  20
-------------------------------------------------------------------------------
 *******************************************************************************
   Input Parameters:

   MAX N. OF CYCLES:                              50
   CONV ON ENERGY:                         1.0000E-05
   PAIR DISTANCE: WEAK                     2.0000E+00
                  DISTANT                  2.0000E+00
   PAOs-COEF TOLL:                         1.0000E-02
   WFs-COEF  TOLL:                         1.0000E-02
   ADJ. GTF EXP. FOR P(g) TRUNCATION       4.0000E-02
   SCHWARZ TOL STRONG WEAK DISTANT: 10-     8   8   8
   DSCREEN TOL STRONG WEAK DISTANT: 10-     8   8   8
   MONKHORST SHR. FACTORS:                  8   8   8
   LEVEL OF PRINTING:                             1
   EXCLUDE PAOs WITH NORM LESS THAN:10-           1
   DOMAINS DEFINED BY INPUT (aggiungere la keyword?)
 *******************************************************************************
```

Note that:

- the tolerance on the energy convergence is tight (anyway, it can be modified by the KW `CONTOL`);
- the meaning of `PAIR` (PAIR DISTANCE) is discussed in depth below;
- the WnF- and PAO- coefficient truncations are set to 10^{-2} (KW `TOBJ`, as previously explained) which corresponds to rather poor tolerances (for **LiH**, the much better level 10^{-3} is adopted);
- the adjoined GTF exponent (k-word `PGNEW`), used in the recalculation of the one-electron density matrix for generating PAOs, is set to 0.04, which corresponds to high accuracy;
- the domains are defined by input (KW `MOLDOM`, the default being `DOMCOE`, as used here for **LiH**);
- the other parameters are more technical (see the Manual for information).

***** Information on WnFs *****
Basic information on the symmetry adapted WnFs provided by the *Properties* part of CRYSTAL is next reported, as shown below for the case of **ACE**.

```
 ********************************************************************************
 WF INFORMATION

-------------------------------------------------------------------------------
 bunch  flower  flower  petal |  type      atom   g   atom   g
          abs     rel         |
-------------------------------------------------------------------------------
   1       1       1      10  |  ATOMIC    C  2  12
                              I              0.0011  0.3718  0.2109  0.0029
   1       2       2      14  |  ATOMIC    C  1   1
                              I              0.0011  0.3718  0.2109  0.0029
   1       3       3      13  |  ATOMIC    C  4   1
                              I              0.0011  0.3718  0.2109  0.0029
   1       4       4      16  |  ATOMIC    C  3   4
                              I              0.0011  0.3718  0.2109  0.0029
   1       5       5      15  |  ATOMIC    C  6   1
                              I              0.0011  0.3718  0.2109  0.0029
   1       6       6      19  |  ATOMIC    C  5   1
                              I              0.0011  0.3718  0.2109  0.0029
   1       7       7      17  |  ATOMIC    C  8  18
                              I              0.0011  0.3718  0.2109  0.0029
   1       8       8      11  |  ATOMIC    C  7   2
                              I              0.0011  0.3718  0.2109  0.0029
                          ------------------------------------------------------
   2       9       1       1  |   BOND     C  6   1   C  2  12
                              I              0.0007  0.3130  0.1829  0.0050
   2       9       1       2  |   BOND     C  6   1   C  2  12
                              I              0.0007  0.3130  0.1829  0.0050
   2       9       1       7  |   BOND     C  6   1   C  2  12
                              I              0.0007  0.3130  0.1829  0.0050
   2      10       2      12  |   BOND     C  5   1   C  1   1
                              I              0.0007  0.3130  0.1829  0.0050
   2      10       2      18  |   BOND     C  5   1   C  1   1
                              I              0.0007  0.3130  0.1829  0.0050
   2      10       2      20  |   BOND     C  5   1   C  1   1
                              I              0.0007  0.3130  0.1829  0.0050
   2      11       3       5  |   BOND     C  8  18   C  4   1
                              I              0.0007  0.3130  0.1829  0.0050
   2      11       3       6  |   BOND     C  8  18   C  4   1
                              I              0.0007  0.3130  0.1829  0.0050
   2      11       3       9  |   BOND     C  8  18   C  4   1
                              I              0.0007  0.3130  0.1829  0.0050
   2      12       4       3  |   BOND     C  7   2   C  3   4
                              I              0.0007  0.3130  0.1829  0.0050
   2      12       4       4  |   BOND     C  7   2   C  3   4
                              I              0.0007  0.3130  0.1829  0.0050
   2      12       4       8  |   BOND     C  7   2   C  3   4
                              I              0.0007  0.3130  0.1829  0.0050
-------------------------------------------------------------------------------
```

Since in **ACE** there are 40 electrons per cell, the total number of WnFs is 20.
The symmetrization procedure generates *two* bunches of SAWnFs.
Bunch #1 comprises 8 single-petal flowers which transform into each other through space-group operation. They are classified as of `ATOMIC` type, and are associated to the 8 carbon atoms. In fact, they correspond to the CH bonds but, since most of the charge is on the carbon atom, this bonding character is not recognized (this would happen by setting the variable TOLB, activated by the KW TOLBON, to a larger value than the default, e.g. 0.4).
Bunch #2 comprises 4 three-petal flowers. Each flower is centered in the middle of the bond of one of the 4 molecules, and its three petals describe the triple bond. The type of these SAWnFs is obviously `BOND`. It is possible in this case to better clarify the

meaning of the symmetry labels. Consider for instance the last WnF:

```
  2      12       4       8  |   BOND     C  7   2   C  3   4
                             I              0.0007  0.3130  0.1829  0.0050
```

This WnF belongs to bunch #2, and to flower #12 (in a total counting) and #4 (within its bunch); it is found at the 8-th place in a list including the 20 WnFs. The two atoms involved in the bond (the *main atoms* of this WnF) are C #7 in the crystal cell #2 and C #3 in the crystal cell #4.
For each WnF, the participation (according to a Mulliken partition) of the various shells of its main atoms in its definition is provided in the line below. For instance, in the first WnF (bunch #1, flower # 1, petal #20), which has only one main atom (C #2 in the crystal cell #12), the participation of the 4 shells of C #2 are 0.0011, 0.3718, 0.2109, 0.0029, showing that this WnF has a hybrid *sp* character.

The case of **LiH** is much simpler in the present respect, since it has only two valence electrons per cell, hence only one WnF (of atomic type, and centered in H, essentially of *s* character):

```
  1       1       1       1  |  ATOMIC    H  1   1
                             I              0.0858  0.1675  0.7537  0.0000 0.
```

Information on the shape of WnF domains is next reported. Since all petals in the same flower have the same domain, this information concerns the different flowers.

Consider first the case of **ACE**:

```
*** FLOWERs DOMAINs ***

 FLOW n.  1
 Atom  2 C    -   n. of G:   1   -->   12
 Atom  6 C    -   n. of G:   1   -->    1
 Atom 10 H    -   n. of G:   1   -->   12
 Atom 14 H    -   n. of G:   1   -->    1

 FLOW n.  2
 Atom  1 C    -   n. of G:   1   -->    1
 Atom  5 C    -   n. of G:   1   -->    1
 Atom  9 H    -   n. of G:   1   -->    1
 Atom 13 H    -   n. of G:   1   -->    1

 FLOW n.  3
 Atom  4 C    -   n. of G:   1   -->    1
 Atom  8 C    -   n. of G:   1   -->   18
 Atom 12 H    -   n. of G:   1   -->    1
 Atom 16 H    -   n. of G:   1   -->   18

 ......

 FLOW n. 11
 Atom  4 C    -   n. of G:   1   -->    1
 Atom  8 C    -   n. of G:   1   -->   18
 Atom 12 H    -   n. of G:   1   -->    1
 Atom 16 H    -   n. of G:   1   -->   18

 FLOW n. 12
 Atom  3 C    -   n. of G:   1   -->    4
 Atom  7 C    -   n. of G:   1   -->    2
 Atom 11 H    -   n. of G:   1   -->    4
 Atom 15 H    -   n. of G:   1   -->    2
```

Since the KW MOLDOM has been used, the domain of each of the 12 flowers coincides in this case with the molecule to which its main atoms belong. For instance, the domains of flowers #8 and #11 coincide, because they are located on the same molecule.

For the case of **LiH**, the output is as follows:

```
*** FLOWERs DOMAINs ***

 FLOW n.  1
 Atom  1 H    -   n. of G:  13   -->    1  3  13  9  7  5  10  11  4  6
                                           8  12  2
 Atom  2 Li   -   n. of G:   6   -->    8  12  2  40  26  30
```

Here, the KW DOMDEF has been used. From the input, we see that just one domain has to be defined; the WnF #1 is involved (the only one!), to which three stars of neighbors are assigned; they are specified in the following card: star #1, which contains one H atom, star #2, which contains six Li atoms, star #3, which contains twelve H atoms, for a total of 19 atoms. The list of the atoms of either type in the domain, and the crystal cell to which they belong are reported.

***** Classification of WnF pairs *****

As previously said, PAIR serves to classify WnF pairs according to the distance (Dist) between the corresponding core domains. This classification concerns in fact pairs of WnF *flowers*, since the domains of all WnFs in a flower coincide. Also, only the symmetry irreducible pairs are classified.
In the case of **ACE**, the core domain is either the C atom to which the CH bond belongs (for "atomic" WnFs), or the two bound C atoms (for "bond" WnFs), and we have set from input: dist1 = 2 Å, dist2 = 8 Å. The part of the output which reports the classification by distance is as follows:

```
 Strong pairs:        3
 Weak pairs:          7
 Distant pairs:       9

 n. of irr-pairs classified:       19

    Flower-Flower Pairs summary
 ------------------------------------------------------------------------------
 pair |    f1    f2    ig | np1 np2 |   Dist    DistC   |  Type |    Integrals
 ------------------------------------------------------------------------------
    1 |     1     1     1 |  1   1  |  0.0000   0.0000 | Strong| Exact
    2 |     1     9     1 |  1   3  |  0.0000   1.2964 | Strong| Exact
    3 |     9     9     1 |  3   3  |  0.0000   0.0000 | Strong| Exact
    4 |     1     3     1 |  1   1  |  3.2886   3.7387 |  Weak | Exact
    5 |     1     5     1 |  1   1  |  1.1372   2.4944 |  Weak | Exact
    6 |     1     8     1 |  1   1  |  3.0980   3.4502 |  Weak | Exact
    7 |     1    11     1 |  1   3  |  3.9336   4.7133 |  Weak | Exact
    8 |     1    12     1 |  1   3  |  3.8784   4.6621 |  Weak | Exact
    9 |     3     9     1 |  1   3  |  3.0980   3.1529 |  Weak | Exact
   10 |     9    10     1 |  3   3  |  3.8784   3.9373 |  Weak | Exact
   11 |     1     2     1 |  1   1  |  4.8462   5.6172 |Distant| Multipolar
   12 |     1     6     1 |  1   1  |  4.8016   5.4295 |Distant| Multipolar
   13 |     1    10     1 |  1   3  |  4.8016   5.0726 |Distant| Multipolar
   14 |     1     1     2 |  1   1  |  5.5682   6.1020 |Distant| Multipolar
   15 |     1     5     2 |  1   1  |  4.9921   5.0874 |Distant| Multipolar
   16 |     1     9     2 |  1   3  |  5.1617   5.1615 |Distant| Multipolar
   17 |     3     2     2 |  1   1  |  5.3656   5.7997 |Distant| Multipolar
   18 |     3    10     2 |  1   3  |  5.7211   6.5340 |Distant| Multipolar
   19 |     9     9     2 |  3   3  |  5.5241   6.1020 |Distant| Multipolar
 ------------------------------------------------------------------------------
```

There are three strong pairs ($d = 0$), seven weak pairs ($0 < d \leq$ dist1), nine distant pairs (dist1$< d \leq$ dist2), for a total of 19 irreducible pairs. Pairs separated by more

than dist2 are considered *very distant*, and they are neglected in the local approach. The table provides information on the pairs considered: the label which identifies each pair (pair), the first (f1) and second (f2) flower involved, the number of the cell where the latter is located (ig) [the first flower is always in the reference "1" cell], the number of petals (np1 and np2) of each flower. Apart from the distance between the two core domains (Dist), also the distance between the respective centers (DistC) is reported. For instance, pair #2 involves an atomic flower (1 petal) and a bond flower (3 petals) belonging to the same molecule. For them, Dist=0, DistC=1.2964 Å, half the length of the C≡C bond. Finally their classification according to distance (Type) and the way the respective integrals are treated (Integrals) are reported. Concerning this point, it can be observed that strong and weak pairs are always treated in the same approximation, so that this distinction is purely formal for the moment being. In the present case, since the DFITTING option has not been activated, these integrals are evaluated exactly, while in the **LiH** case, they are calculated with the DF technique. On the contrary, the integrals of distant pairs are evaluated in a multipolar approximation, because in both cases the MULTIPO option has been activated.

***** SCF information *****
The SCF MP2 calculation is next started.
Cycle by cycle, the contribution to the MP2 correlation energy from each pair is reported, along with the total energy.
This is exemplified below for the case of **ACE** (first cycle):

```
  Cycle number     1

----------------------|-----------------------------------------------
       pair deg petals |    ecorr         e2            e2 grimme
----------------------|-----------------------------------------------
@@      1    8   1      |   -0.02349892   -0.02351009   -0.02819870
@@      2   16   3      |   -0.01497798   -0.01441493   -0.01249024
@@      3    4   9      |   -0.13324567   -0.12853852   -0.13285143
@@      4   48   1      |   -0.00001406   -0.00001393   -0.00001082
@@      5    8   1      |   -0.00046131   -0.00041999   -0.00038185
@@      6   48   1      |   -0.00002349   -0.00002356   -0.00001826
@@      7   48   3      |   -0.00002082   -0.00001951   -0.00001601
@@      8   48   3      |   -0.00002201   -0.00002067   -0.00001691
@@      9   48   3      |   -0.00011116   -0.00010614   -0.00008839
@@     10   48   9      |   -0.00010512   -0.00009339   -0.00008167
@@     11   48   1      |   -0.00000141   -0.00000137   -0.00000108
@@     12   48   1      |   -0.00000158   -0.00000153   -0.00000121
@@     13   48   3      |   -0.00000584   -0.00000539   -0.00000448
@@     14   48   1      |   -0.00000068   -0.00000067   -0.00000052
@@     15   24   1      |   -0.00000177   -0.00000175   -0.00000135
@@     16   48   3      |   -0.00000455   -0.00000426   -0.00000349
@@     17   48   1      |   -0.00000095   -0.00000094   -0.00000072
@@     18   48   3      |   -0.00000244   -0.00000229   -0.00000187
@@     19   24   9      |   -0.00000914   -0.00000817   -0.00000701
----------------------|-----------------------------------------------
    Cycle   Delta       |    ecorr         e2            e2 grimme
@I@   1      -0.02908339 |   -0.97965131   -0.95056792   -0.97187614
```

This table provides the local MP2 correlation energy for each pair. deg is the degeneracy of the pair due to the symmetry classification, petals is the product of the number of petals of the two flowers. ecorr and e2 are the pair correlation energies at the given SCF cycle: the latter includes the contribution of the residues, the former not (see equation 7 of Ref. 1); at convergence, the two must coincide. e2 grimme is the correlation energy obtained after a straightforward correction according to the Grimme method[14]. The sum of the contributions from the different pairs of flowers multiplied by the respective degeneracy (deg) is reported in the last line. Delta = ecorr - e2 gives an indication of the distance from convergence.

The corresponding section of the ouput for the last cycle of the **LiH** calculation is as follows:

```
  Cycle number     3
----------------------|-----------------------------------------
      pair deg petals |    ecorr         e2            e2 grimme
----------------------|-----------------------------------------
@@     1    1   1      |   -0.02392389   -0.02392476   -0.02870867
@@     2   12   1      |   -0.00046675   -0.00046675   -0.00036717
@@     3    6   1      |   -0.00008184   -0.00008184   -0.00006416
@@     4   24   1      |   -0.00002373   -0.00002373   -0.00001841
@@     5   12   1      |   -0.00001152   -0.00001152   -0.00000895
@@     6   24   1      |   -0.00000515   -0.00000515   -0.00000397
@@     7    8   1      |   -0.00000270   -0.00000270   -0.00000208
@@     8   48   1      |   -0.00000169   -0.00000169   -0.00000130
@@     9    6   1      |   -0.00000103   -0.00000103   -0.00000079
@@    10   24   1      |   -0.00000071   -0.00000071   -0.00000055
@@    11   12   1      |   -0.00000072   -0.00000072   -0.00000055
@@    12   24   1      |   -0.00000052   -0.00000052   -0.00000040
@@    13   24   1      |   -0.00000038   -0.00000038   -0.00000029
@@    14   24   1      |   -0.00000029   -0.00000029   -0.00000022
@@    15   48   1      |   -0.00000023   -0.00000023   -0.00000017
@@    16   24   1      |   -0.00000023   -0.00000023   -0.00000017
@@    17   48   1      |   -0.00000015   -0.00000015   -0.00000011
@@    18   12   1      |   -0.00000012   -0.00000012   -0.00000009
@@    19   24   1      |   -0.00000010   -0.00000010   -0.00000008
----------------------|-----------------------------------------
    Cycle   Delta      |    ecorr         e2            e2 grimme
@I@   3     0.00000079 |   -0.03103997   -0.03104076   -0.03429214
```

It can be noticed that `ecorr` and `e2` coincide within the assigned tolerance (`CONTOL`=0.00001), and the calculation is terminated.

B.2 Lennard-Jones contribution

```
.....................................................................

  Lennard-Jones extrapolated energy contributions:

   LJ(MP2)             -0.0000861623   LJ(GRIMME)               -0.0000660520

   HF ENERGY       -8.0592434162E+00
   HF+MP2+LJ EN    -8.0593295785E+00   HF+GRIMME+LJ EN.      -8.0593094681E+00

  WARNING: with the chosen tolerance on energy, for at least one fl-fl type all
  g-stars have been used to calculate L-J contributions.

.....................................................................
```

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Index

AMPREA, 12
ASYMDOM, 12

CONTOL, 8
COREQ, 8
COVVV, 12

DELPAO, 8
Density Fitting, 12
DENSMAT, 11
DF performance, 14
DFCHECK, 14
DFITTING, 13
DFSCHW, 13
DOMCOE, 9
DOMDEF, 10
DOMDEF2, 10
DOMONLY, 15
DOMPUL, 9
DOMREA, 15
DSCREEN, 12

END, 7, 8
ENVPAIR, 15
EQALG, 11

FIXDOM, 15
FIXNPAOS, 15
FORCE, 7
Freezing of Indices, 15

Gilat net, 8

Input example, 16
Input instructions, 4
INTREA, 12

LENJONES, 11
Local periodic MP2 theory, 2
LONTOL, 8

MAXDOM, 9
MEMORY, 8
MINPOP, 9
MOENPAIR, 15
MOLATOMS, 15
MOLDOM, 10
MOLPAIR, 15
Monkhorst net, 8
MP2 equations, 11
MP2OLD, 11
MPREAD, 12
MULTDIST, 12
MULTIPO, 12
Multipolar Expansion, 12

NEWK, 8
NOSYM12, 11
NPAOSREA, 15

OPERTOL, 8
Output examples, 19
OVLMETR, 13

PAIR, 8
PCALC, 11
PGNEW, 8
Plotting option, 11
POLECORR, 13
PRINPLOT, 11
Printing option, 11

SCHWARZ, 12
SELECINT, 14
STAR, 8
STARDSTR, 10
Symmetry adapted WF, 6
SYMMFLAG, 7
SYMMWF, 7
SYMVER, 7

TESTDOM, 10
Tests, 23
TOBJ, 8
TOLBON, 7
TOLEAMPS, 11
TOLEQPRS, 11
TOLPRO, 7
TOLSHL, 7
Truncation criteria, 8
Truncation tolerances, 8

Two-electron integrals, 12

WPROJE, 8